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(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 0 974 571 A2

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:

26.01.2000 Bulletin 2000/04

(51) Int Cl.7: **C07C 17/25**

(21) Application number: 99305781.9

(22) Date of filing: 21.07.1999

(84) Designated Contracting States:

**AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE**

Designated Extension States:

AL LT LV MK RO SI

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(54) **Preparation of 1,1,1,3-tetrafluoropropene(1234ze)**

(57) Disclosed is a process for the preparation of cis/trans 1,1,1,3-tetrafluoro-2-propene (1234 ze) which comprises (a) contacting 1,1,1,3,3-pentafluoropropane (245fa) with an alkaline solution, preferably an aqueous

or alcoholic solution of a base such as KOH, NaOH, Ca (OH)₂ or Mg(OH)₂, or with a chromium-based catalyst, such as fluorided Cr₂O₃ or fluorided Cr/Ni/AlF₃, and (b) recovering cis/trans 1,1,1,3-tetrafluoro-2-propene from the reaction mixture.

EP 0 974 571 A2

Description

[0001] This invention relates to preparation of cis/trans 1,1,1,3-tetrafluoropropene ("1234ze"), a monomer useful for the preparation of various homopolymers and copolymers, particularly to processes for the dehydrofluorination of 1,1,1,3,3-pentafluoropropane ("245fa"), a known blowing agent, to 1234ze using a chromium-based catalyst or a strong base. While the prior art, R. N. Haszeldine, J. Chem. Soc., 1952 (3490), describes the synthesis of cis/trans 1,1,1,3-tetrafluoropropene by fluorination of 1,1,1-trifluoro-2-propyne, this latter feed stock material is not available commercially.

[0002] Herein provided is a process for the preparation of 1234ze which comprises

- (a) contacting 245fa with an alkaline solution or with a chromium-based catalyst, and
- (b) recovering cis/trans 1,1,1,3-tetrafluoro-2-propene from the resulting reaction mixture.

[0003] It has now been discovered that the cis and trans isomers of 1,1,1,3-tetrafluoro-2-propene (1234ze) can be conveniently prepared by dehydrofluorination of the blowing agent, 245fa, using either a strong base (either an aqueous or alcoholic solution) or a chromium-based catalyst.

[0004] The catalyzed process is preferably carried out in the gas phase. Use of an oxygen-containing gas such as air is desired to extend the catalyst lifetime, the level of oxygen generally being from about 1 to about 10 volume percent (preferably about 2 to 5%), based on the volume of the organic feed. Temperatures of from about 100°C. to about 600°C. are typically used, preferably from about 300°C. to about 400°C. The pressure can be atmospheric. Contact time (total flow rate per catalyst volume) is typically from about 1 to about 60 seconds, preferably from about 20 to 50 seconds. The catalyst is a chromium-based catalyst such as fluorided chromium oxide, Cr_2O_3 , which chromium-based catalyst is either unsupported or supported on a support such as activated carbon, graphite, fluorided graphite or fluorided alumina, the chromium catalyst being used alone or in the presence of a co-catalyst selected from a nickel, cobalt, manganese or zinc salt. Two such preferred chromium catalysts are high surface area chromium oxide and chromiuminickel on fluorided alumina ($\text{Cr}/\text{Ni}/\text{AlF}_3$), preparation of this latter catalyst being taught, for example, in European Patent 486333. The chromium-based catalysts are preferably activated before use, typically by a procedure wherein the catalyst bed is heated to about 370°-380°C. (normally with a continuous flow of nitrogen), after which a mixture of approximately equal volumes of HF and air or nitrogen (preferably nitrogen) are fed over the catalyst bed for about 18 hours.

[0005] The dehydrofluorination can also be accomplished using an alkaline solution of a strong base, such as an aqueous or alcoholic solution of potassium hy-

droxide (KOH), sodium hydroxide (NaOH), calcium hydroxide ($\text{Ca}(\text{OH})_2$) or magnesium hydroxide ($\text{Mg}(\text{OH})_2$). For the alcoholic solution, a conventional alcohol such as ethanol can be used. The solution typically is from about 0.01 to about 10 molar, preferably 0.1 to 5 molar. The dehydrofluorination is typically conducted at a temperature of from about 20°C. to about 100°C., preferably from about 20°C. to about 50°C.

[0006] The following examples are illustrative.

[0007] Example 1. 52.4 Grams of a high surface area Cr_2O_3 catalyst was activated by first feeding 30 ccm of nitrogen for 2 hours at 370°C. followed by cofeeding 30 ccm of HF and 30 ccm of nitrogen for 18 hours at 370°C. Subsequently, a mixture of 20 ccm of 245fa and 3 ccm of air (equal to about 3 volume % of oxygen, based on the 245fa volume) was fed over the catalyst bed at 400°C for a contact time of 45 seconds. Conversion was 96.2%. Selectivity for the desired (1234ze) product was about 96.3% (about 18.5% cis, about 77.8% trans). Performance of the catalyst was steady for 360 hours.

[0008] Example 2. Example 1 was repeated using $\text{Cr}/\text{Ni}/\text{AlF}_3$ catalyst (activated at 370°C. using a cofeed of 30 ccm of nitrogen and 30 ccm of HF for 18 hours) in a series of 3 tests, using the same temperature and air/245fa feed ratio, but with the contact time between 26 and 39 seconds. Conversions ranged from 88 to 94.5%. Selectivity for the desired (1234ze) product ranged from 96.2 to 98.5% (17.7 to 20.5% cis, 77 to 80.5% trans).

[0009] Example 3. 10 ccm of 245fa was bubbled through 3000 ml of 2.7 molar KOH solution at room temperature (about 20°C.). Analysis of the gaseous dry product, using gas chromatography on line, showed 26% conversion, with selectivity for the desired (1234ze) product of 97.9% (23.9% cis, 74% trans).

Claims

1. A process for the preparation of cis/trans 1,1,1,3-tetrafluoro-2-propene which comprises (a) contacting 1,1,1,3,3-pentafluoropropane with an alkaline solution or with a chromium-based catalyst, and (b) recovering cis/trans 1,1,1,3-tetrafluoro-2-propene from the resulting reaction mixture.
2. A process for the preparation of cis/trans 1,1,1,3-tetrafluoro-2-propene which comprises (a) contacting 1,1,1,3,3-pentafluoropropane with an aqueous or alcoholic solution of base selected from the group consisting of potassium hydroxide, sodium hydroxide, calcium hydroxide or magnesium hydroxide, and (b) recovering cis/trans 1,1,1,3-tetrafluoro-2-propene from the resulting reaction mixture.
3. A process as in Claim 2 wherein step (a) comprises contacting 1,1,1,3,3-pentafluoropropane with an aqueous potassium hydroxide solution.

4. A process for the preparation of cis/trans 1,1,1,3-tetrafluoro-2-propene which comprises (a) contacting 1,1,1,3,3-pentafluoropropane with an oxygen-containing gas in the presence of a fluorided catalyst selected from Cr_2O_3 or Cr/Ni/AlF_3 , and (b) recovering cis/trans 1,1,1,3-tetrafluoro-2-propene from the resulting reaction mixture.
5. A process as in Claim 4 wherein the catalyst is fluorided Cr_2O_3 .
6. A process as in Claim 4 wherein the catalyst is fluorided Cr/Ni/AlF_3 .

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alcohol was removed by distillation, 20 ml. of water was added and the mixture was extracted several times with ether. The aqueous solution was acidified with sulfuric acid and distilled; the distillate was made alkaline and evaporated to dryness. The residue was converted to isobutyro-*p*-toluidide, m. p. 103.5–104.5°. From the ether extracts there was obtained 0.8 g. of isobutyryl-mesitylene, b. p. 140–143° (20 mm.), n_D^{20} 1.5086, which was converted to α ,3,5-tribromo-2,4,6-trimethylisobutyrophenone, m. p. 106–107°.

Summary

Tetramethyl-1,3-cyclobutanedione has been found to undergo cleavage of the ring when treated with organic magnesium and lithium compounds. The behavior of this cyclic β -diketone has been found to be strictly analogous to the behavior of open-chain β -diketones with these reagents.

BATON ROUGE, LOUISIANA RECEIVED AUGUST 10, 1945

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AT THE OHIO STATE UNIVERSITY]

Fluorinated Derivatives of Propane and Propylene. VI

BY ALBERT L. HENNE AND T. PHILLIP WAALKES

Electron diffraction measurements have shown that atomic distances are shrunk in polyfluorinated groups. This shrinkage is not restricted to the carbon-fluorine distance, but also affects the carbon to chlorine distance in CCl_2F_2 , or the carbon to carbon distance in CF_3CH_3 . To understand the behavior of polyfluorides, it would be well to learn how far this effect extends down a chain, whether the effect of two polyfluorinated groups is cumulative, and what the influence is on a double bond. For such purposes, the synthesis of $\text{CF}_3\text{CH}_2\text{CF}_3$, $\text{CF}_2=\text{CHCF}_3$, $\text{CH}_2=\text{CFCF}_3$, and $\text{CF}_2=\text{CFCF}_3$ was undertaken; these compounds were chosen in the hope that their electron diffraction patterns would not be too complicated to resolve. They were sent to Dr. L. O. Brockway at the University of Michigan, who will report the electron diffraction measurements.

The syntheses have used operations which have all been described in our previous papers.^{1,2,3} All intermediates have been isolated and characterized as single, definite individuals. Great care was given to criteria of purity, for which whole freezing curves, not merely freezing points, were used. Compounds were regarded as adequately purified only after their freezing range had become as small as indicated in the table of physical constants.

Experimental

Synthesis of $\text{CF}_3\text{CH}_2\text{CF}_3$.—The sequence of reactions found most convenient was: $\text{CH}_3\text{CHClCHCl}_2 \rightarrow \text{CH}_3\text{CH}=\text{CCl}_2 \rightarrow \text{CH}_3\text{CH}_2\text{CFCl}_2$ and $\text{CH}_3\text{CH}_2\text{CF}_2\text{Cl} \rightarrow \text{CH}_3\text{CH}_2\text{CF}_3 \rightarrow \text{CCl}_3\text{CH}_2\text{CF}_3 \rightarrow \text{CF}_3\text{CH}_2\text{CF}_3$. The starting point was commercial $\text{CH}_3\text{CHClCHCl}_2$, which an alkaline treatment transformed into $\text{CH}_3\text{CH}=\text{CCl}_2$ with an 88% yield. The latter, heated with hydrogen fluoride⁴ at 100° as long as a 20 atm. pressure could be maintained while bleeding off the generated hydrogen chloride, gave an average yield of 60% of $\text{CH}_3\text{CH}_2\text{CF}_2\text{Cl}$ and 12% of $\text{CH}_3\text{CH}_2\text{CFCl}_2$. The passage from $\text{CH}_3\text{CH}_2\text{CF}_2\text{Cl}$ to $\text{CH}_3\text{CH}_2\text{CF}_3$ was easily brought about, in 90% yield, by means of

nascent mercuric fluoride⁵; an alternate method, calling for dehydrohalogenation to $\text{CH}_3\text{CH}=\text{CF}_2$, followed by hydrogen fluoride addition, was found less practical, as its first step proved time-consuming. The trifluoropropane was chlorinated to $\text{CF}_3\text{CH}_2\text{CCl}_3$, in the manner shown before,⁶ and the latter upon treatment with nascent mercuric fluoride⁵ yielded the desired $\text{CF}_3\text{CH}_2\text{CF}_3$ (84%), together with some intermediate $\text{CClF}_2\text{CH}_2\text{CF}_3$, (5%).

Synthesis of $\text{CF}_2=\text{CHCF}_3$.—The hydrogen atoms in $\text{CF}_3\text{CH}_2\text{CF}_3$ (obtained as shown in the preceding paragraph) are exceedingly acid in character,⁷ and the compound is therefore very easily attacked by alcoholic potassium hydroxide. The action of the alkali removed only hydrochloric acid, as shown by a positive test for chlorine ions and a negative test for fluorine ions. The reaction was both intramolecular, for a 65% yield of $\text{CF}_2=\text{CHCF}_3$, and intermolecular as shown by the appearance of condensation products boiling about 70 and 105°, respectively.

When hydrogen fluoride was added to $\text{CF}_2=\text{CHCF}_3$, practically no $\text{CF}_3\text{CH}_2\text{CF}_3$ was formed at temperatures below 100°, but at 100° or higher the addition proceeded smoothly and quantitatively.

Synthesis of $\text{CH}_2=\text{CFCF}_3$.—The following sequence was used: $\text{CH}_3\text{ClCHClCH}_2\text{Cl} \rightarrow \text{CH}_2=\text{CClCH}_2\text{Cl} \rightarrow \text{CH}_3\text{CFCICH}_2\text{Cl} \rightarrow \text{CH}_2\text{CFCICHCl}_2 \rightarrow \text{CH}_3\text{CFCICF}_2\text{Cl} \rightarrow \text{CH}_2=\text{CFCF}_3$. The fluorine atom on the central carbon was introduced first. For that purpose, the starting point was commercial $\text{CH}_3\text{ClCHClCH}_2\text{Cl}$, which a caustic treatment transformed into $\text{CH}_2=\text{CClCH}_2\text{Cl}$ in 80% yield. The addition of hydrogen fluoride proceeded normally to give about 70% of $\text{CH}_3\text{CFCICH}_2\text{Cl}$, with $\text{CH}_3\text{CF}_2\text{CH}_2\text{Cl}$ as by-product.⁸ Directed chlorination in sunlight gives the expected $\text{CH}_3\text{CFCICHCl}_2$. At this stage, our original plans called for an alkaline treatment to remove hydrogen chloride and yield $\text{CH}_2=\text{CFCHCl}_2$, in which the transformation of the CCl_2 group into a CF_2 was expected to be facilitated by its "allylic" character.⁹ However this dehydrohalogenation (and also that of $\text{CH}_3\text{CCl}_2\text{CCl}_3$) failed, because the hydrolysis of $\text{CH}_2=\text{CXCCl}_2$ is much faster than its generation. To avoid this decomposition, partial fluorination of the saturated compound was resorted to, which yielded a mixture of 10% $\text{CH}_3\text{CFCICFCl}_2$, 35% $\text{CH}_3\text{CFCICF}_2\text{Cl}$ and 35% $\text{CH}_3\text{CF}_2\text{CFCl}_2$, separable by distillation. After accumulating $\text{CH}_3\text{CFCICF}_2\text{Cl}$, the alkaline treatment was applied, and yielded very slowly (three days) the desired $\text{CH}_2=\text{CFCF}_3$, which proved stable enough to resist hydrolysis. In view of the time consumed, the dehydrohalogenation was then tried on $\text{CH}_3\text{CFCICFCl}_2$. When operated under a reflux condenser maintained at about 50°, the olefin $\text{CH}_2=\text{CF}_2$

(1) Henne in Gilman's "Organic Chemistry," Vol. I, John Wiley and Sons, New York, 1943, p. 944.

(2) Henne in "Organic Reactions," Vol. 2, John Wiley and Sons, New York, 1944, p. 42.

(3) Henne and Waalkes, THIS JOURNAL, 67, 1639 (1945).

(4) Henne and Plueddemann, *ibid.*, 68, 1271 (1942).

(5) Henne, *ibid.*, 60, 1569 (1938); Henne and Flanagan, *ibid.*, 65, 2362 (1943).

(6) Henne and Whaley, *ibid.*, 64, 1157 (1942).

(7) Henne, Hinkamp and Zimmerschied, *ibid.*, 67, 1906 (1945).

(8) Henne and Haackl, *ibid.*, 63, 2892 (1941).

(9) Henne, Whaley and Stevenson, *ibid.*, 68, 2478 (1941).

March, 1946

FLUORINATED DERIVATIVES OF PROPANE AND PROPYLENE

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TABLE I
PHYSICAL CONSTANTS

Compounds	F. p., °C.	F. p., °C.	B. p., °C.	d_4^{20}	n_D^{20}	M. R. ^a	A. R. F. ^b
CH ₂ =CH=CF ₂	0.1	-160.93	-29.0
CF ₂ Cl-CH ₂ -CF ₂	.1	-107	28.4	1.4372	1.2875	21.07	1.13
CF ₂ =CH-CF ₂	.2	-153.11	-21.0
CF ₂ -CH ₂ -CF ₂	.1	-93.62	-0.7
CH ₂ -CFCI-CF ₂ Cl	.4	-30.48	55.6	1.3956	1.3503	25.77	1.09
CH ₂ =CF-CFCl ₂	.4	-115.9 ± 0.2	54.4	1.3523	1.3851	25.48	1.13
CH ₂ =CF-CF ₂ Cl	.4	-143.7	11.9
CH ₂ =CF-CF ₂	.2	-152.24	-28.3
CHCl=CF-CCl ₂	...	Glass	147.8	1.5877	1.4870	35.84	0.77
CHCl=CF-CF ₂	.2	-115.8	15.0
CCl ₂ =CF-CCl ₂	2.0	-77	171.1	1.7064	1.5026	40.21	1.39
CCl ₂ =CF-CF ₂	0.2	-139.6	46.4	1.5389	1.3504	25.60	1.17
CFCI ₂ -CFCI-CF ₂	...	Glass	73.5	1.6643	1.3529	30.92	1.13
CFCI=CF-CF ₂	5.0	-158	7.9
CF ₂ Cl-CFCI-CF ₂	1.0	-136	34.7	1.5896	1.3029	26.21	1.17
CF ₂ =CF-CF ₂	0.4	-156.2	-29.4
CFCI=CCl-CF ₂	.3	-137	47.3	1.5468	1.3511	25.52	1.15
CF ₂ -CFCI-CF ₂	...	Glass	-2.0
CF ₂ CCl ₂ CCl ₂ F	...	+41.74	112.4

^a M. R. is the molecular refraction $\frac{M}{d} \cdot \frac{n^2 - 1}{n^2 + 2}$. ^b A. R. F. is the atomic refraction for fluorine, computed by subtracting from M. R. the customary increments for C, H, Cl and double bond.

CFCI₂ distilled out as soon as formed and escaped hydrolysis; this procedure gave about 40% of olefin, and 40% of recovered paraffin which was retreated. Both CH₂=CFCFCI₂ and CH₂=CFCF₂Cl underwent "allylic" fluorination with antimony fluoride in the customary fashion, to yield the desired CH₂=CFCF₂.

Synthesis of CF₂=CFCF₂.—A practical sequence was as follows: CH₃CFCICH₂Cl → CHCl₂CFCICCl₂ → CCl₂=CF-CCl₂ → CCl₂=CFCF₂ → CCl₂CFCICF₂ → CF₂CICCFICF₂ → CF₂=CFCF₂. First, commercial CH₃CICH₂CH₂Cl was transformed into CH₃CFCICH₂Cl, as in the preceding paragraph. This was subjected to chlorination but in such a way⁸ as to yield a mixture of CHCl₂CCIFCCl₂ and CH₂CICCFICCl₂, from which an alkaline treatment easily gave a mixture of CCl₂=CFCCl₂ and CHCl=CFCCl₂.^{9,10} The two olefins, on "allylic" fluorination⁹ with antimony trifluoride yielded the expected CHCl=CFCF₂ and CCl₂=CFCF₂, both of which were transformed quantitatively into CCl₂CCIFCF₂ by the intensive action of chlorine. This fully chlorinated compound was then fluorinated with SbF₃Cl₂ at 180° to yield about 60% CF₂CICFCICF₂ and 28% CFCI₂CFCICF₂. The last step, zinc treatment of CF₂CICFCICF₂ to yield CF₂=CFCF₂, proved very slow (three days) in boiling alcohol, but was conveniently carried out under pressure at 100°.

Side-line Reactions.—(a) CH₃CICH₂CF₂ was dehydrohalogenated to yield CH₂=CHCF₂. b. p. -19 to -17°.

(b) CH₃CFCICF₂Cl was treated with zinc but failed to yield more than traces of CH₂CF=CF₂ even at 200°.

(c) CFCI₂CCl₂CF₂ was synthesized from CCl₂CCl₂CF₂ and antimony trifluoride. It was then quantitatively dechlorinated with zinc to CFCI=CClCF₂. Fluorine was

added to the double bond by means of the lead dioxide + hydrogen fluoride process⁹ to yield CF₂CICFCICF₂, from which more CF₂=CFCF₂ was prepared as shown above.

(d) CF₂CICCl₂CF₂⁹ was dehalogenated with zinc to CF₂=CClCF₂, and the latter subjected to fluorine addition⁹ as in the preceding paragraph, to yield CF₂CFCICF₂.

(e) Hydrogen fluoride addition was tried on a series of olefins. Successful additions were observed with CH₃CH=CF₂ and CF₂=CHCF₂; failures occurred with CHCl=CFCCl₂; CH₂=CFCFCl₂; CH₂=CFCF₂Cl; CH₂=CFCF₂.

Physical Constants.—All compounds were purified in the manner shown in our previous papers,¹¹ and their physical constants were measured¹¹ with the precision denoted in Table I. In this table, the freezing range is that between incipient crystallization and inability further to stir the mass. M. R. is the molecular refraction calculated by means of the Lorenz-Lorentz formula, and A. R. F. is the atomic refraction for fluorine computed by subtracting from M. R. the customary increments for C (2.418), H (1.100), Cl (5.967) and double bond (1.733).

Analysis.—Analyses for chlorine were performed at convenient stages in the various syntheses; the percentages calculated and found were as follows: CF₂CICH₂CF₂, 21.0 and 20.7; CH₃CFCICF₂Cl, 42.4 and 41.4; CH₂=CF-CFCI₂, 48.2 and 47.8; CCl₂=CFCCl₂, 76.3 and 75.9; CCl₂=CFCF₂, 37.9 and 37.5; CFCI=CFCCl₂, 72.0 and 70.3; CFCI₂CFCICF₂, 44.8 and 44.4.

Summary

For the purpose of interatomic distance measurements a series of new fluorinated derivatives of propane and of propylene have been prepared. Their physical constants were measured after intensive purification and are tabulated.

COLUMBUS, OHIO

RECEIVED SEPTEMBER 17, 1945

(11) Henne and Hinkamp, THIS JOURNAL, 67, 1194 (1945).

(10) It proved important to prevent the chlorination from reaching the CCl₂CFCICCl₂ stage, because the latter could not be transformed into CCl₂=CFCCl₂ by a zinc treatment and was therefore a total loss; in the zinc treatment much decomposition occurs and an impure product is obtained which seems to contain fluoropentachlorocyclopropane.